

CRYOGENIC ENGINEERING, PRODUCTION AND USE OF INDUSTRIAL GASES

CRYOGENIC TECHNOLOGIES BASED ON STIRLING MACHINES FOR LIQUEFIED BIOMETHANE PRODUCTION

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A promising avenue of research into creation of alternative motor fuels and their use in motor transport is production of a new type of motor fuel, namely, liquefied (cryogenic) biomethane (LBM) and its use in internal combustion engines of motor vehicles.

The feedstock for production of gaseous biomethane is biogas, the chief source for whose production, in turn, are municipal (sewer) gases and droppings of domestic animals and poultry. Biogas is a mixture of methane and carbon dioxide, a product of methane fermentation of organic matters of vegetables and animals, which is brought about by a specific natural biotic community of bacteria of various physiological groups. Methane fermentation occurs between 10 and 55°C in three distinct ranges: 10–25°C – psychrophilic (cold-loving), 25–40°C – mesophilic (warmth-loving), and 52–55°C – thermophilic (heat-loving); the humidity range is 8–99%, the optimum being 92–93%. The methane content in the biogas varies in the range 50–90%, depending on the chemical composition of the feedstock. Depending on the nature of the original source, the biogas yield varies from 200 to 600 liter per ton of absolutely dry matter. Presently, a variety of biogas production technologies has been developed and is in use. These are based on use of different variations of temperature conditions, humidity, concentration of the bacterial mass, duration of bioreactions, etc.

Biogas produced from animal wastes generally contains 60–70% methane, 30–35% carbon dioxide, 2–3% nitrogen, 1–2% hydrogen, and up to 1% oxygen. In this case, its volume combustion heat is not higher than 20–22 MJ/m³, i.e., **1 m³ of biogas is equivalent to 0.55 kg of diesel oil.**

Biogas produced from municipal waste gases and droppings of domestic animals can itself be directly used as motor fuel.

The main sources of biogas are sewer gases and biogas from domestic animal and poultry droppings.

Sewer (aeration) gases: these are products of fermentation of waste waters of town sewer representing a variety of biogas that contains 60–65% methane, 30–35% carbon dioxide, and 2–4% hydrogen. Practical experience shows that the yield of sewer gases from a treatment station fed by a sewer network serving population centers of more than 100,000 people attains more than 2500 m³ a day, which is equivalent to 2000 liters of gasoline [1].

Considering that the population of large cities of Russia is generally more than 500,000, sewer gases are becoming a real source of alternative motor fuel in these cities. For instance, autotransportation facilities of St. Petersburg can daily get as much as 100,000 m³ of biogas, which will allow a considerable part of the city autotransport to be switched over to alternative motor fuel, saving 80,000 liters of oil products (gasoline and diesel) per day.

One of the biogas sources is **poultry farms**. At present, for large poultry farms in Russia, it is promising to produce biogas by anaerobic fermentation of organic wastes in specially made installations, so-called methane tanks (anaerobic methane digesters), using methane-forming bacteria.

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In methane tanks, the process is accomplished most efficiently at a fermentation temperature of 52–55°C (thermophilic condition). The fermented mass is an excellent sterilized organic fertilizer with a high content of nutrients.

For the purpose of determination of biogas yield, it may be assumed that in a typical poultry farm there are 25,000 fowls yielding droppings of up to 5 tons/day, from which 5000 m³ of biogas can be produced. So, from 1 ton of fowl droppings motor fuel equivalent to 800 liters of gasoline can be produced.

In the USSR, experiments on biogas production from fowl droppings were performed at the October Poultry Plant of the Glebov Poultry Association.

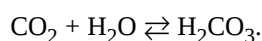
No less important as a biogas source is **livestock farming**. The fact that domestic animals (cows, horses, sheep, pigs, etc.) poorly assimilate energy of vegetable feeds and more than half of the solar energy accumulated in these feeds by photosynthesis is used unproductively as being lost as dung allows the latter to be treated not only as a valuable raw material for organic fertilizers but also as a powerful renewable energy source. As with poultry droppings, biogas production from wastes of domestic animals is based on the use of anaerobic dung fermentation process in methane tanks. During fermentation, in the dung grows microflora, which gradually degrades the organic matters to acids, and the latter, being attacked by syntrophic and methane-forming bacteria, are converted to gaseous products, viz., methane and carbon dioxide. From 1 ton of dry dung, by anaerobic fermentation under optimum conditions, 350 m³ of biogas can be produced, which, on conversion to one cattle, is 2.5 m³ per day or roughly 900 m³ per year [2]. Calculating the biogas equivalent to conventional motor fuel, **at a first glance, quite a paradoxical fact can be established that one cow, besides milk, provides about 700 liters of gasoline** a year.

Simultaneously, in the process of fermentation of the dung, the latter is deodorized and disinfested from parasitic worms, the germinating capacity of the seeds of weeds is destroyed, and the fertilizing matters are converted to mineral form. In this regard, it must be noted that the technology of biogas production by anaerobic fermentation in methane tanks is the most economic means of processing of organic wastes of poultry and livestock farms into dry fertilizer.

However, creation of internal combustion engines running on a low-calorie (combustion-heat) gas, which the biogas is, faces specific difficulties arising from the need to maintain the power and efficiency of operation of the basic engine under the operating conditions, to maintain the reliability of the engine, to assure stability in all conditions and minimal design modification of the basic engine, etc. **So, it is more advisable to use biomethane derived from the biogas rather than the biogas itself.** For this purpose, carbon dioxide and other impurities are removed from the biogas, after which the obtained gas is practically uniform in composition and contains 90–97% methane with a volume combustion heat of 35–40 MJ/m³ and an octane number of 110. As a result, in terms of characteristics of a motor fuel, biomethane is superior to even natural gas.

Biogas may be rid of carbon dioxide by various means whose choice depends on the efficiency of the bioenergy installation, location of the installation, etc. The most common methods are purging of the gases through liquid absorbents like water, freezing, and low-temperature adsorption [3].

Let us examine one of the above-referred methods. Although solubility of carbon dioxide in water is not high, this is the cheapest way to remove it from biogas. The method is based on dissolution of the carbon dioxide in a washing liquid with virtually no chemical reaction (absorption process). At 0°C, 1.7 volume part of carbon dioxide is dissolved in one volume part of water. Dissolution of carbon dioxide in water is an exothermic process, so its solubility diminishes with rise in temperature. For instance, at 20°C only 0.88 volume part of carbon dioxide is dissolved in one volume part of water. Solution of carbon dioxide in water has a sourish taste and a weakly acidic reaction due to presence in the solution of small quantities of carbonic acid formed as a result of the reversible reaction



The equilibrium of the latter reaction strongly shifts leftward because a very small quantity of the dissolved carbon dioxide converts to carbonic acid.

In carbon dioxide removal from biogas with water, methane loss is negligible because methane is almost insoluble in water. For instance, in 100 ml of water, not more than 5.5 ml of methane is dissolved at 0°C and 3.3 ml methane, at 20°C. The carbon dioxide content in the biogas can be reduced roughly to 0.4–0.6% by washing with water under pressure.

Biomethane, like any other gaseous fuel, has a low volume energy concentration. Under normal conditions, the volume combustion heat of biomethane is 33–36 kJ/liter, whereas the volume combustion heat of gasoline is 31,400 kJ/liter, i.e., 1000 times higher. So, biomethane can be used in automobiles as a motor fuel either in a compressed or in a liquefied (cryogenic) state.

Sewer biomethane as a motor fuel was first used in the fall of 1946 in a trial run of 18 bottled-gas driven motor vehicles on the Berlin–Kiev–Moscow route. Of the 18 gas vehicles, 13 ran on liquefied propane-butane and five, on compressed biomethane obtained by cleaning sewer gases from carbon dioxide and compressing to 20 MPa. The biomethane contained as much as 90% methane and had a volume combustion heat of 31,425 kJ/m³ and an octane number of 110. Later, in Czechoslovakia, the USA, and other countries, motor vehicles were tested after conversion for running on compressed sewer biomethane. The tests confirmed its suitability as a motor fuel.

Research on use of **compressed biomethane from poultry droppings** as a motor fuel for automobile transport was conducted in the USSR as well in the mid-eighties of the last century. For the study of the major characteristics of biomethane and the performance of road tests, an experimental bottled-gas driven automobile, Moskvich-2140, fitted with a standard fuel equipment designed to compress the gas to 20 MPa was built [4]. The tests proved that in using compressed biomethane, by special control of the gas equipment, the same parameters as those of natural gas can be obtained. The pickup and maximum speed of the light vehicle running on biomethane remained at the previous level. Further, it was proved that the efficiency of gas-driven vehicle is higher than that of the gasoline-driven at low speeds.

As a motor fuel, biomethane has a higher antiknock rating than petroleum motor fuels, which makes it possible to lower the concentration of deleterious matters in the exhaust gases of internal combustion engines and to reduce the amount of deposits in the engine. Since there is no liquid phase, the oil film is not washed out from the engine cylinder, the wear of the parts of the cylinder–piston group diminishes two folds, and, consequently, the reliability and life of the engine increases. Analysis of the research data obtained abroad on toxicity of bottled-gas motor vehicles has shown that when gasoline is replaced by biomethane, depending on the type of the motor vehicle, discharge of toxic matters into the town atmosphere diminishes 5–10 times in terms of carbon dioxide, three times in terms of hydrocarbons, 1.5–2.5 times in terms of nitrogen oxides, 10 times in terms of polyaromatic hydrocarbons, and 8–10 times in terms of exhaust smoke.

The major factor restraining wide use of compressed biomethane as a motor fuel, as in the case of compressed natural gas, is transportation of the substantial dead load of the bottles.

An usual 40-liter metallic bottle under a pressure of 15 MPa contains about 6 m³ or 4.3 kg of biomethane. The container mass is as much as 70–80 kg, i.e., the share of the useful load (gas) is only 5.5% of the total mass of a filled bottle. On an average, for a truck with a load capacity of 4.5 ton, the consumption of biomethane is about 250 g/km, i.e., one bottle of gas is enough for a run of 16 km. With four bottles, the truck run may be raised to 60–70 km.

Use of compressed biomethane in mobile agricultural engineering is also difficult because of low mass–dimension ratios of the fuel systems and of the difficulty in accommodating the bottles in tractors without impairing their agroengineering indices, especially for row-crop tractors (Belarus-type) and ploughing caterpillar tractors. In addition, use of compressed biomethane does not provide for necessary spare supply of motor fuel for peak periods during sowing and harvesting operations. For tractor engineering, the hourly consumption of natural gas is 4–5 kg, accounting for the fact that a compressed biomethane bottle contains only 4.3 kg of gas. A tractor with four bottles can run for more than 3–4 h. If the compression pressure is raised, the bottle mass rises roughly in proportion to the density of the compressed gas, which is why it is impossible to substantially reduce by such method the mass of the compressed gas storage system.

Quite a bit of inconveniences and difficulties fall off on conversion to liquefied biomethane (LBM). Liquefaction makes it possible to reduce the volume of the gas occupied in usual conditions almost by 600 times and store it at virtually atmospheric pressure, and thus to reduce the mass of the fuel system in the automobile 3–4 times and the volume, 2–3 times vis-à-vis compressed biomethane.

The cycle of research and design work carried out at the Military Space Engineering University demonstrated that use of LBM for automobile and tractor parks may be organized as follows. For this, a cryogenic tank of up to 150-liter capacity with appropriate fixtures is installed in a ZIL-130 type of automobile or a Belarus type of tractor. The mass of the cryogenic tank with the fixtures is not more than 170 kg. The LBM is supplied from the tank to the vaporizer coil wound on the

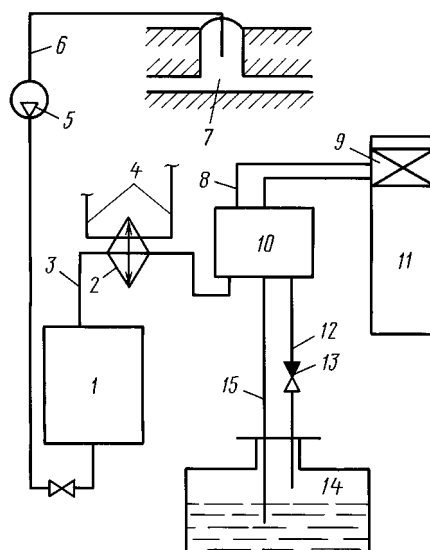


Fig. 1. Schematic diagram of liquefying installation for LBM production based on Stirling technology.

exhaust pipe of the engine. The heat of the exhaust gases vaporizes the LBM, which runs into the mixer, and from there, in the form of methane–air mixture, into the engine cylinder. Thus, installation of a 150-liter (62 kg) cryogenic LBM tank on a tractor makes it possible to significantly extend the duration of operation of the tractor between refillings. Calculations show that at an average consumption of about 5 kg/h, this volume of LBM suffices for 12 h of uninterrupted running.

For a ZIL-138A type of truck converted to biomethane and fitted with a 300-liter cryogenic tank, the run on a single filling increases 1.8 times, and the total mass of the equipment and fuel diminishes by 570 kg in comparison with the same automobile running on compressed biomethane.

However, up until now there is no simple and economically viable gaseous biomethane liquefaction technology, owing to which LBM has not been used in internal combustion engine earlier.

In the present economic situation, only emergence of a relatively inexpensive method of LBM production may make this form of fuel competitive in the domestic motor fuel market.

The results of a series of theoretical and experimental work carried out in developing the concept of liquefied natural gas (LNG) production for the automobile transport of the Russian Federation, which is based on the application of the Stirling technology, helped develop a new unique LBM production technology [5–7].

The Stirling technology is founded on the idea of creation of gaseous biomethane liquefaction installations based on cryogenic gas machines (CGM) running on the Stirling cycle. Domestic and foreign Stirling CGMs are cryogenerators based on the principle of external cooling and designed to liquefy gases whose condensation point is not lower than 70 K (–200°C). Stirling CGM is most effective at 111 K (–162°C), i.e., at the temperature at which phase transition of the gaseous biomethane into liquid occurs.

The gaseous biomethane being liquefied is not subjected in the machine to compression and does not come into contact with the moving parts of the machine and the lubricant, so the liquid product (LBM) is clean and fully meets the specifications TU (Technical Specification) 51-03-03-85 and the GOST (State Standard) 27.577–87 for motor fuel.

In Fig. 1, we show the schematic diagram of the liquefying installation that realizes the method of production of cheap and ecologically clean fuel, LBM, from sewer gases.

The liquefying installation operates as follows. Aerated biogas from the sewer channel 7 (or methane tank in case of domestic animal and poultry droppings) is fed by the compressor 5 through the biogas supply line 6 into cleaning unit 1 where the gas is cleaned from carbon dioxide. Thereafter, the gas with the residual impurities flows through the line 3

into the freezing unit 10 where the impurities (H_2O , CO_2) of the obtained biomethane are frozen. In the condenser 9 of the Stirling cryogenic machine 11, the dry clean biomethane flowing through the line 8 liquefies on account of external cooling and passes under gravity into the LBM storage tank 14 through the drainage line 15. In order to maintain equal pressure in the gas chamber of the LBM storage tank 14 and in the condenser 9, which allows draining of the liquefied gas from the condenser 9 into the tank 14 under gravity, a provision has been for a connecting piece 12 with a check valve 13 which connects the gas chamber of the tank 14 with the freezing unit 10. To cool the methane-containing gas in the cooling heat exchanger 2, there is a provision for an external heat carrier line 4 with the temperature of the surrounding medium, for instance of atmospheric air.

Independent expert technoeconomic appraisal made by the specialists of the St. Petersburg Fund for Supporting Military-Industrial Complex (VPK) has shown that liquefied methane-containing motor fuels based on the Stirling technology are highly profitable. For instance, based on preliminary estimates, the cost of 1 liter of LBM, with due regard for conversion of the automobile to LBM, will not be higher than 1.5 rubles. In this case, the pay-back time for the expenses for the liquefying installations based on Stirling CGM is less than two years. Currently, a demonstration pilot plant for liquefaction of biomethane and natural gas, based on Stirling CGM ZIF-700, is under construction in St. Petersburg.

Thus, LGM produced from sewer gases and from domestic animal and poultry wastes by the Stirling technology is the cheapest and ecologically cleanest local motor fuel with quick expense recovery, which allows replacement of conventional petroleum fuel (gasoline and diesel oil) in internal combustion engines.

Use of Stirling CGM will make it possible to build high-efficiency liquefying installations for production of LBM of the desired productivity which is costwise affordable to a large part of the autoindustry in Russia and will make use of LBM as a motor fuel as simple and easy as use of conventional petroleum fuels.

Note that the bottled-gas equipment of automobiles running on LBM fully conforms to the automobiles running on liquefied natural gas. This fact will make it possible, if necessary, to make equitable substitution of LBM with liquefied natural gas and vice versa. This will allow creation in a short time a single infrastructure for production and servicing of automobile and tractor engineering of the Russian Federation with alternative motor fuels, namely, liquefied natural gas (LNG) and liquefied biomethane (LBM).

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